

# PATENT SPECIFICATION

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- (72) Inventors FREDERIK C. VAN DE VLASAKKER and  
 MARTINUS A. VAN GEMERT



## (54) ANAEROBIC COMPOSITIONS WITH PLASTIC FLOW CHARACTERISTICS

(71) We, LOCTITE CORPORATION, a corporation organised under the laws of the State of Connecticut, United States of America, located at 705 N. Mountain Road, City of Newington, County of Hartford, State of Connecticut, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to anaerobic compositions having plastic flow characteristics.

Anaerobic compositions are catalysed, polymerisable mixtures which generally function as adhesives or sealants for the joining of non-porous surfaces. A prime reason for the great popularity of these compositions is their unique inhibition mechanism. As long as the compositions remain in contact with adequate amounts of oxygen, such as atmospheric oxygen, polymerisation or cure of the composition will not commence even though the composition contains a significant amount of a room temperature polymerisation initiator.

When the anaerobic composition is placed between surfaces which are relatively impervious to oxygen, however, the stabilising effect of the atmospheric oxygen is removed and cure commences within a relatively short time. The products are conventionally sold in partially empty, low-density polyethylene bottles. As the bottle is pervious to atmospheric oxygen, the liquid is continuously contacted by fresh oxygen through the bottle walls and from the air space in the bottle. As a result, it is possible to precatalyse a polymerisable composition which can be used as a single component sealant or adhesive, and still have the composition remain in the stable, uncured state for periods of one year or longer prior to use.

In recent years considerable effort has been devoted to adaption of anaerobic compositions and their accompanying technology to production line applications. This has taken the form of both application techniques, principally application equipment specifically designed to handle anaerobic compositions, and modification of the anaerobic compositions to render them more useful at production line speeds. For example, high viscosity or thixotropic anaerobic compositions have been prepared in an attempt to develop anaerobic systems which have greater capacity for retention on parts to which they are applied. These increases in viscosity and thixotropy have been obtained by the use of both organic materials such as organic polymers and inorganic compounds such as silica. Compositions of these types are described, for example, in our copending application No. 52403/71 (Serial No. 1362407). These compositions have not been totally satisfactory since under commonly experienced temperature changes and mechanical shock, such as vibration and normal handling procedures, even high viscosity or thixotropic materials are likely to flow from the parts to which they have been applied to some extent, reducing the bonding or sealant efficiency, and raising the possibility of flow of composition to an undesirable area.

More recent attempts have involved the preparation of non-flowable anaerobic compositions, such as anaerobic compositions in sheet or waxlike form. Compositions of this type are disclosed, for example, in United States Patents 2,547,851 and 3,625,875. Such compositions exhibit many of the properties of solid or semi-solid systems, such as melting or transition from the solid to the liquid state over a relatively

narrow temperature range. While these systems offer substantial advantages in the area of retention on the part to which they are applied, they have not been very easy to apply and frequently have produced reduction in certain properties, such as shear strength, solvent resistance and heat resistance of the cured product.

An anaerobic composition which could be applied to parts destined for assembly, which was capable of being retained on the parts with little or no migration therefrom, and which retained the bulk of the cured properties of conventional liquid anaerobic compositions, would be a major advance in the area of parts assembly via adhesives and sealants.

This present invention provides an anaerobic composition having a yield point and hence plastic flow characteristics, i.e. which is gelled and non-flowable when at rest but can be turned into a flowable liquid with the input of modest amounts of mechanical energy. More particularly the composition comprises a polymerisable acrylate ester monomer, a peroxy polymerisation initiator capable of polymerising the ester at room temperature in the substantial absence of oxygen, silica or a hydrated silica-alumina clay having an average particle size of 2 microns or less (frequently hereinafter referred to as "silica and silica clay"), and a polar coupling agent for the said silica or hydrated silica-alumina clay having at least two active hydrogen atoms, the anaerobic composition having a yield point of at least 100 dynes per square centimetre.

The invention also provides a process for the production of an anaerobic composition as defined above which comprises uniformly distributing the silica or hydrated silica-alumina clay and the polar coupling agent therefor in the remaining components of the anaerobic composition, and allowing the mixture to stand until it forms a gel-like substance.

The invention also provides an article for assembly with a mating second article at least a portion of the engagement area of the article being coated with an anaerobic composition as defined above.

As indicated above, silica-type materials have been used as thickening agents or thixotropic agents in anaerobic compositions previously, but have been generally found to be less satisfactory than organic polymeric thickeners and thixotropic agents since, inter alia, high levels of the silica-type materials have had adverse effect on the stability and/or speed of cure of the anaerobic composition, and presented significant processing problems during manufacture. Further, it has not hitherto proved possible to prepare anaerobic compositions possessing plastic flow characteristics. The fact that such compositions can be prepared is surprising in that the flow and diffusion characteristics of liquids, which have been felt to supply oxygen to anaerobic compositions for stability, no longer exist.

The composition of this invention, in contrast to the conventional prior art liquid anaerobic composition, is gelled and non-flowable when at rest, and hence will not flow from a part to which it is applied. This remains the case even under modest inputs of mechanical energy or normally encountered temperature changes. The yield point (the measure of input of mechanical energy which first commences laminar flow within the anaerobic composition) is at least 100 dynes per square centimetre, and preferably at least 200 dynes per square centimetre. This will ensure that the anaerobic composition remains in the gelled and non-flowable state under normal handling conditions. Naturally, under conditions of higher inputs of mechanical energy, such as transportation on vibratory conveyors, higher yield points are desirable. Rarely, however, will the yield point need to be above about 400 dynes per square centimetre to prevent flow under handling conditions, and hence it is highly preferred that the yield point for the compositions according to the invention be above this level.

At the higher level, the yield point is generally a question of convenience, although if exceptionally high yield point values are achieved it may become difficult to work with the anaerobic composition and return it to its liquid state. The maximum yield point level is generally 10,000 dynes per square centimetre, preferably 7,000 dynes per square centimetre, and most preferably 5,000 dynes per square centimetre.

Once the yield point has been exceeded and the anaerobic composition has liquefied, it is preferred that the viscosity drop as rapidly as possible to a freely flowable state. In this manner, the adaptability of the anaerobic composition to automatic application is simplified. Preferably, the composition exhibits a high shear viscosity between 1,000 and 100,000 centipoise, more preferably between 1,500 centipoise and 50,000 centipoise, and most preferably between 2,000 and 25,000 centipoise. As used herein, "high shear viscosity" refers to the equilibrium viscosity of the liquid measured under high shear conditions, such as the Brookfield viscosity at 30 revolutions per minute and 25°C.

The first additive necessary to produce the yield point anaerobic compositions of

this invention is silica or a hydrated silica-alumina clay. Silica ( $\text{SiO}_2$ ) is a common inorganic chemical available under a variety of trade names and in a variety of forms. The hydrated silica-alumina clays are available with a wide variety of molecular structures, all of which have silica and alumina ( $\text{Al}_2\text{O}_3$ ) as common structural components. Some of these compositions contain only hydrated silica and alumina (such as kaolinite and pyrophyllite), while others have included within their structure salts or complexes of other metals, such as magnesium (montmorillonite) or sodium (bentonite). While these materials are complex in structure, they do form a well recognized class of clay materials and are well known to those skilled in the art.

To be useful in the compositions of this invention, the silica or hydrated silica-alumina clay should have an average particle size of 2 microns or less, and preferably 1 micron or less. Most preferably, particularly in dealing with silica, the particle size is less than 0.1 microns. With these small particle sizes, the surface area per unit weight of the silica and silica clay becomes quite high and the efficiency in forming a yield point at relatively low concentrations is increased.

The coupling agent added to form the anaerobic compositions according to the invention, is a polar compound containing at least two active hydrogen atoms capable of entering into the coupling reaction with the silica or hydrated silica-alumina clay. The common classes are water and organic compounds containing at least two hydroxyl or primary or secondary amine groups. Preferably the organic compounds contain from 2 to 4 hydroxyl or primary or secondary amine groups, and preferably do not contain more than 10 carbon atoms. Examples of suitable diol and diamine compounds are ethyleneglycol, propyleneglycol, 1-3 butyleneglycol, glycerol, NN'-dimethyl ethylene diamine, NN'-dimethyl, propylene diamine, diethanol amine and triethanolamine.

The silica or silica clay is generally used within the range of 2% to 10% by weight of the anaerobic composition, and preferably from 2.5% to 7%. The coupling agent generally is used in an amount of from 10% to 50% by weight of the silica or silica clay. Higher levels can be used without deleterious effect, but also without significant benefit. To avoid deleterious effect to the anaerobic composition, the coupling agent should not exceed about 5% by weight of the anaerobic composition, and should preferably not exceed about 4%. A preferred lower limit is about 0.3% by weight of the anaerobic composition.

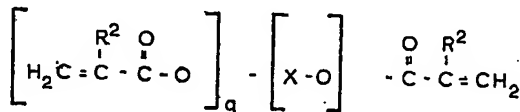
It is preferred to use no more of these two additives than is necessary to form the yield point anaerobic composition of this invention, since higher use levels can adversely affect the strength and other desirable properties of the cured sealant or adhesive. Optimum levels of the additives will vary somewhat from one system to the next, depending upon the specific ingredients of the anaerobic composition. With the above-described use ranges as specific guides, a minimum of routine testing will easily determine the optimum use levels for the silica or silica clay and coupling agent therefore in any anaerobic composition.

As indicated above, the anaerobic composition has as required elements a polymerisable monomer and a peroxy initiator therefor which is latent in the presence of oxygen, but which is capable of polymerising the monomer at room temperature within a reasonable period of time after removal of the inhibiting effect of oxygen.

The monomers for use in the anaerobic compositions are polymerisable acrylate esters. When used in the composition of this invention, preferably at least a portion of the acrylate monomer is a di- or other polyacrylate ester. These poly-functional monomers produce cross-linked polymers, which serve as more effective and more durable sealants and adhesives.

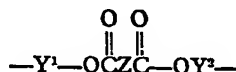
The polyacrylate esters may be represented by the formula

(1)



wherein each  $\text{R}^2$  is a hydrogen or a halogen atom or an alkyl group with from 1 to 4 carbon atoms;  $q$  is an integer equal to at least 1, and preferably equal to from 1 to 4; and  $\text{X}$  is an organic radical containing at least two carbon atoms and having a valency of  $q$  plus 1. With regard to the upper limit for the number of carbon atoms in " $\text{X}$ ", workable monomers exist at essentially any value. As a practical matter, however, a general upper limit is about 50 carbon atoms, preferably 30, and most preferably 20.

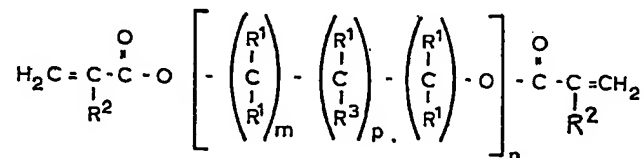
For example, X can be an organic radical of the formula



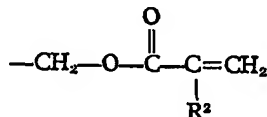
wherein each of  $Y^1$  and  $Y^2$  is an divalent organic radical, preferably a hydrocarbon group, containing at least 2 carbon atoms, and preferably from 2 to 10 carbon atoms, and Z is a divalent organic radical, preferably a hydrocarbon group, containing at least 1 carbon atom, and preferably from 2 to 10 carbon atoms. Other classes of useful polyacrylate ester monomers are the isocyanate-monoacrylate reaction reproducts described in United States Patent 3,425,988 and the reaction products of di- or tri-alkylolamines (e.g. ethanolamines or propanolamines) with acrylic acids, such as are disclosed in French Patent No. 1,581,361.

The most highly preferred acrylate esters which can be used in the compositions according to the invention are polyacrylate esters which have the following general formula:

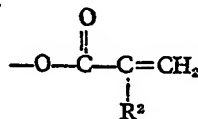
(2)



wherein each  $R^1$  represents a hydrogen atom, a lower alkyl radical with from 1 to 4 carbon atoms, a hydroxy alkyl radical with from 1 to 4 carbon atoms, or a radical of the formula



each  $R^2$  represents a hydrogen or a halogen atom or a lower alkyl radical with from 1 to 4 carbon atoms; each  $R^3$  represents a hydrogen atom, a hydroxy group or a radical of formula



m is an integer equal to at least 1, e.g. from 1 to 15 and preferably from 1 to 8 inclusive; n is an integer equal to at least 1, e.g. 1 to 40 and preferably from 2 to 10; and p is 0 or 1.

Typical examples of polyacrylate esters corresponding to the above general formula are di-, tri- and tetraethyleneglycol dimethacrylate; di(pentamethyleneglycol) dimethacrylate; tetraethyleneglycol diacrylate; tetraethyleneglycol di(chloroacrylate; diglycol diacrylate; diglycerol tetramethacrylate; butyleneglycol dimethacrylate; neopentylglycol diacrylate; and trimethylolpropane triacrylate.

While di- and other polyacrylate esters and particularly the polyacrylate esters described in the preceding paragraphs, have been found particularly desirable, monofunctional acrylate esters (esters containing one acrylate group) may also be used. When dealing with monofunctional acrylate esters, it is highly preferable to use an ester which has a relatively polar alcoholic moiety. Such materials are less volatile than low molecular weight alkyl esters and, more important, the polar group tends to provide intermolecular attraction during and after cure, thus producing more desirable cure properties, as well as a more durable sealant or adhesive. Most preferably the polar group is a labile hydrogen atom, a heterocyclic ring, or a hydroxy, amino, cyano, or halogen

polar group. Typical examples of compounds within this category are cyclohexyl methacrylate, tetrahydrofurfuryl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, *t*-butylaminoethyl methacrylate, cyanoethyl acrylate, and chloroethyl methacrylate.

As indicated above the anaerobic compositions as discussed herein are prepared by mixing a peroxy initiator with one or more acrylate esters as described above. While certain peroxides (generally dialkyl peroxides) have been disclosed as useful initiators in, e.g. United States Patents 3,419,512 and 3,479,246, the hydroperoxides are highly superior and constitute a highly preferred embodiment.

The real benefit of the non-hydroperoxide initiators is as a co-initiator with the hydroperoxides to make the cure properties of the anaerobic composition more universal.

Hydrogen-peroxide may be used, but the most desirable polymerisation initiators are the organic hydroperoxides. Included within this definition are materials such as organic peroxides or organic peresters which decompose or hydrolyse to form organic hydroperoxides *in situ*. Examples of such peroxides and peresters are cyclohexyl hydroxycyclohexyl peroxide and *t*-butyl perbenzoate, respectively.

While the nature of the organic hydroperoxides is not critical to the broad concept of this invention, the general class of hydroperoxides can be represented by the formula  $R^4OOH$ , wherein  $R^4$  is generally a monovalent hydrocarbon group containing up to 18 carbon atoms, and preferably is an alkyl group with from 3 to 12 carbon atoms or an aryl or aralkyl group containing up to 12 carbon atoms. Naturally  $R^4$  can contain any substituent or linkage, hydrocarbon or otherwise, which does not affect the hydroperoxide adversely for the purpose disclosed herein. Typical examples of such organic hydroperoxides are cumene hydroperoxide, tertiary butyl hydroperoxide, methylethylketone hydroperoxide, and hydroperoxides formed by oxygenation of various hydrocarbons such as methylbutene, cetane, and cyclohexane, and various ketones and ethers, including certain compounds represented by the general formula (2) above.

The organic hydroperoxide initiators can be used within wide ranges, e.g., up to about 20% by weight of the composition. Most commonly, however, they comprise no more than about 10 percent by weight of the composition since above that level adverse effects on the strength and durability of the cured composition may be experienced. While in some instances lower amounts can be used, about 0.1% by weight of the composition is a common lower limit. Preferably the hydroperoxide initiator comprises from 0.1% to 5% by weight of the composition.

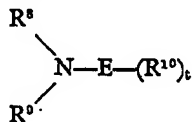
Common additives for anaerobic compositions are latent polymerisation accelerators, compounds which do not of themselves initiate cure, but which accelerate the cure once it has been started by the polymerisation initiator. It should be noted that large numbers of polymerisation accelerators are known in the art, and the broad concept of this invention is intended to encompass any polymerisation accelerator which can be incorporated in the anaerobic composition without destroying the essential characteristics of such composition.

Among the earliest of the polymerisation accelerators used in anaerobic composition were amines. The most commonly used are tertiary amines such as tributylamine and triethylamine. Essentially the entire class of tertiary amines can be used in such compositions, and the class may be broadly represented by the formula



wherein each of  $R^5$ ,  $R^6$  and  $R^7$  is a monovalent hydrocarbon group containing up to about ten carbon atoms. Naturally the hydrocarbon groups can contain any substituent or linkage which does not adversely affect the workability of the amine to perform its intended function. Preferably, each of  $R^5$ ,  $R^6$  and  $R^7$  is an alkyl, aryl or aralkyl group containing up to 8 carbon atoms.

The *N,N*-dialkyl aryl amines are particularly effective tertiary amines. Typical amines within this class may be represented by the following general formula:

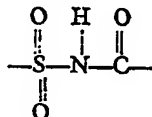


wherein E represents a benzene or naphthalene nucleus;  $R^8$  and  $R^9$  are monovalent hydrocarbon groups containing up to 10 carbon atoms, and preferably are low alkyl radicals of 1 to 4 carbon atoms; *t* is 0 or an integer from 1 to 5 inclusive;  $R^{10}$  is a mono-

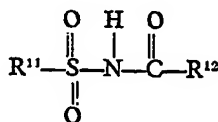
valent hydrocarbon or alkoxy group containing up to 5 carbon atoms, and preferably is a lower alkyl or a lower alkoxy radical with 1 to 4 carbon atoms, provided that when an  $R^{10}$  radical is in the ortho position,  $r$  is greater than 1.

Primary and secondary amines also can be used as accelerators in the anaerobic compositions of this invention. Particularly good primary and secondary amines are the primary and secondary alkyl amines, most particularly those wherein each alkyl group contains up to 10 carbon atoms. A separate and highly preferred class of secondary amines has been found to be the class of heterocyclic secondary amines, particularly heterocyclic secondary amines containing up to 20 carbon atoms. It also is preferred to use those amines wherein the heterocyclic ring is hydrogenated. Typical examples of such compounds are pyrrolidine, piperazine and 1,2,3,4-tetrahydroquinoline.

Another highly successful class of accelerators is the organic sulphimides, i.e., organic compounds which contain the group



Because of the extreme effectiveness of the sulphimides as accelerators for anaerobic compositions, compositions containing sulphimides constitute a highly preferred embodiment of the present invention. While the broad class of organic sulphimides can be used successfully, the sulphimides most commonly used can be represented by the formula



wherein each of  $R^{11}$  and  $R^{12}$  is a monovalent hydrocarbon group containing up to ten carbon atoms, and preferably up to six carbon atoms. Naturally  $R^{11}$  and  $R^{12}$  can contain any linkage or substituent which does not adversely affect the sulphimide for its intended use in the anaerobic composition. Further,  $R^{11}$  and  $R^{12}$  can be united to bond the sulphimide group in a heterocyclic ring, or a polynuclear heterocyclic ring system. Of the organic sulphimides, benzoic sulphimide has been found to be the most preferable.

An even more highly preferred composition is that which contains a sulphimide, particularly benzoic sulphimide, in combination with either a heterocyclic secondary amine or a tertiary N,N-dialkyl aryl amine, both of which are described above. For an expanded discussion of this type of system, reference is made to United States Patent 3,218,305.

Other less active accelerators can be used in the compositions of this invention. Typical examples of such accelerators are succinimide, phthalimide and formamide.

Routine testing will easily determine the optimum amount of accelerator which can be incorporated in any given anaerobic composition. However, the following general guide lines may be used. With regard to tertiary amines, large amounts may be used if desired, up to about 8 percent by weight of the composition, or higher. However, little if any additional benefit is obtained above about 5 percent. Most preferably these tertiary amine accelerators are used in an amount of from 1 percent to 4 percent by weight of the anaerobic composition. The succinimide, phthalimide and formamide accelerators can also be used in significant amounts, up to about 8 percent by weight of the composition, or higher, and preferably from 1 percent to 5 percent by weight. The sulphimide and heterocyclic secondary amine accelerators generally are used at less than about 4 percent by weight of the anaerobic composition. In the special case where a sulphimide is used in combination with a heterocyclic secondary amine or an N,N-dialkyl arylamine, the total of the two accelerators preferably does not exceed about 4 percent by weight of the anaerobic composition, and either component does not exceed about 3 percent by weight.

Other ingredients can be used in the anaerobic compositions of this invention, and in its preferred aspects polymerisation inhibitors are included to offer protection against spurious polymerisation prior to the time of intended use. The quinones have been

found to be a particularly effective class of polymerisation inhibitors. Examples of such quinones are  $\beta$ -naphthaquinone, 2-methoxy-1, 4-naphthaquinone, and *p*-benzoquinone.

5 Other typical ingredients which can be used if desired to impart commercially desirable properties to the composition are thickeners, plasticisers, dyes, adhesive agents and thixotropic agents. Such materials can be used in such combinations and proportions as is desired, provided they do not affect adversely the anaerobic nature of the composition. While exceptions may exist in some cases, these materials *in toto* generally do not comprise more than about 50 percent by weight of the total composition, and preferably not more than about 20 percent by weight of the composition. 10

The above described anaerobic compositions can be prepared by the use of any conventional mixing technique which obtains uniform distribution of the silica or silica clay and the coupling agent throughout the remainder of the composition. While the order of addition is not critical, it has been found preferable to uniformly distribute the silica or silica clay throughout the remainder of the ingredients of the anaerobic composition prior to the addition of the coupling agent. Additionally, it has been found preferable to add the silica or silica clay and coupling agent by the use of high shear mixing, since this optimises the speed and uniformity of the distribution and helps to prevent agglomeration of ingredients which are not readily dispersed. 15

As indicated previously, another aspect of this invention concerns parts or objects for assembly, at least a portion of the engagement areas of which are coated with a yield point anaerobic composition according to the present invention. "Engagement areas" refers to the areas of the parts which mesh or otherwise mate with a second part to which it is to be sealed or bonded. For example, the outer race of a bearing is an engagement area, as this area is mated with a second surface (such as the inside of a hub) to hold the bearing in place. 20

In a particularly preferred embodiment of the invention, the yield point anaerobic composition is coated onto at least a portion of the threaded area of a threaded part, such as a threaded fastener or a threaded pipe. The composition can easily be applied to the threads while in the liquid state, and thereafter will gel, or solidify, in the thread roots to form a pre-applied and durable thread sealing or thread bonding coating. 25

The invention is illustrated by the following examples which are given to demonstrate processes and compositions within the scope of the present invention and are not intended to be limitations in any way upon the scope of the invention. Unless specifically stated to the contrary, all ratios and percentages in the following examples are expressed on a weight basis. All silica and silica clay used in the example had an average particle size less than 2 microns. 30

#### EXAMPLE I

Anaerobic Composition I was prepared having the following approximate composition: 35

	Ingredient	Approx. Wt. %	
	Polyethyleneglycol dimethacrylate (molecular weight=330)	77.8	
	Polyethyleneglycol di-2-ethylhexoate	12.7	
45	Polystyrene	5.3	45
	Cumene hydroperoxide	3.0	
	N,N-diethyl <i>p</i> -toluidine	0.5	
	Benzoic sulphimide	0.4	
	N,N-dimethyl <i>o</i> -toluidine	0.3	
50	$\beta$ -Naphthaquinone	100 parts per million	50

Anaerobic Composition I was a freely flowing liquid with a viscosity at 25°C of about 125 centipoise. To this composition were added with high shear mixing about 5.25% by weight silica and about 0.5% by weight water, the percentages being based on the weight of Composition I, and mixing was continued until a clear, uniform solution resulted. The final mixture was immediately poured into cylindrical containers and allowed to remain at rest. When viewed after one hour, it was found that the compositions had solidified and become non-flowable and gel-like. Cylinders of the "gelled" material 3/4" in diameter were cut 1-1/4" and 1-5/8" long, respectively, and placed upright on a table. These cylinders supported their own weight and did not migrate or liquefy with the passage of time. 55

60

After gelation in a beaker, a portion of the above composition was subjected to rapid stirring; it rapidly assumed a liquid state and could be poured from the beaker in a similar way to a normal liquid. As rapidly mixed, it had an apparent viscosity of approximately 2,000 to 5,000 centipoise.

A sample of the liquefied composition was poured in a beaker and inserted in a Brookfield Model RVT viscometer equipped with a No. 6 spindle. After the material had gelled, or solidified, the viscometer was turned on and the amount of torque applied was noted at the point when the first movement of the spindle was detected. From this torque figure, it was calculated that the liquid withstood a shear force of approximately 550 dynes per square centimetre before flow commenced. All of the above tests confirm that plastic flow characteristics had been imparted to Anaerobic Composition I, thus forming a composition within the scope of the present invention.

A sample of the above composition was stirred until it liquefied, and was then applied in the liquid state to the threads of a series of standard black oxide bolts. It was noted that within a short time the liquid material assumed a gelled, or solidified, state in the threads of the bolt. The bolt could be moved and vibrated without affecting the position or texture of the composition in the thread roots. Mating nuts were thereafter assembled onto the coated portion of the bolt. The assembly was completed easily without the use of significant force, i.e. essentially no resistance to the nut was observed. After 15 minutes, 60 minutes and 24 hours from the time of assembly, the average torque required to move the nut relative to the bolt through one revolution was determined. The torques were respectively: 18 kg-cm, 100 kg-cm, and 100 kg-cm, respectively.

The composition was subjected to room temperature ageing and accelerated ageing at 82°C. In each case the composition was found to retain the shelf-stable characteristics of conventional anaerobic compositions, i.e., the composition remained in the uncured state in a partially empty bottle. Thereafter the composition would cure rapidly when placed in the substantial absence of air, such as on the threads of a standard nut and bolt.

#### EXAMPLE II

An anaerobic composition was prepared with essentially the same composition as in Example I, above, except that the silica was replaced by an equivalent amount, i.e. an amount such as to provide the same amount of hydrated silica, of montmorillonite (a hydrated silica-alumina clay) sold under the name of "Bentone-27" (Bentone is a Trade Mark). Substantially identical results were achieved in that a stable anaerobic composition possessing a yield point was obtained.

Second and third anaerobic compositions were prepared, each with the same composition as in Example I, above, except that the second anaerobic composition additionally contained 0.15% by weight glycerin and the third additionally contained 0.15% by weight ethyleneglycol. Substantially identical compositions of this invention possessing yield points were produced, except that the compositions of this Example were of a slightly more firm gel than in Example I, and slightly greater amounts of mechanical energy (e.g., stirring) were required to liquefy the compositions.

#### EXAMPLE III

Anaerobic Composition II was prepared having the following approximate composition:

	Ingredient	Approx. Wt. %	
	Polyethyleneglycol dimethacrylate as in Example I	68.3	
50	Bisphenol-A-fumarate	28.5	50
	Cumene hydroperoxide	2.0	
	Benzoic sulphimide	0.4	
	N,N-diethyl-p-toluidine	0.5	
55	N,N-diethyl-o-toluidine	0.3	55
	$\beta$ -Naphthaquinone	100 parts per million	

This composition was a conventional free flowing liquid with an approximate viscosity at 25°C of 500 centipoise. Under high shear mixing, 4-1/4% silica and 0.5% water by weight were added, the percentages being based on the weight of Composition II. The composition, after remaining at rest, formed a firm non-flowable gel-like substance, similar to that described in Example I, above. The non-flowable gel



could be broken and the system converted to a readily flowable liquid by rapid mixing in a beaker. When returned to rest, the composition reverted to the non-flowable structure. One inch high cylinders of the gelled material 1" and 3/4", respectively in diameter would support their own weight without flow. When applied to the threads of a bolt, the composition would readily re-solidify to its gelled state and would not be moved from the thread roots under moderate mechanical vibration and handling.

The composition of this Example was stirred to liquefy it, and was then coated onto standard black oxide bolts in the test described in Example I. When tested after 15 minutes, 60 minutes, and 24 hours, the required torques were 10, 245, and 344 kg-cm respectively.

Portions of the composition were heat aged at 82°C, or aged at room temperature. Each sample retained its anaerobic characteristics, e.g., remained in the uncured state when stored in partially empty bottles, but cured when thereafter placed in the substantial absence of oxygen, such as between the threads of a mated nut and bolt.

#### WHAT WE CLAIM IS:—

1. An anaerobic composition which is gelled and non-flowable when at rest comprising a polymerisable acrylate ester monomer, a peroxy polymerisation initiator capable of polymerising the ester at room temperature in the substantial absence of oxygen, silica or a hydrated silica-alumina clay having an average particle size of 2 microns or less, and a polar coupling agent for the said silica or hydrated silica-alumina clay having at least two active hydrogen atoms, the anaerobic composition having a yield point of at least 100 dynes per square centimeter.

2. A composition as claimed in claim 1, containing from 0.1 to 20% by weight of an organic hydroperoxy polymerisation initiator.

3. A composition as claimed in Claim 2 containing from 0.1% to 10% by weight of organic hydroperoxy initiator.

4. A composition as claimed in any of claims 1 to 3 containing from 2% to 10% by weight of silica or hydrated silica-alumina clay.

5. A composition as claimed in claim 4 containing from 2.5% to 7% by weight of silica or hydrated silica-alumina clay.

6. A composition as claimed in any of claims 1 to 5 containing from 0.3% to 5% by weight of the polar coupling agent for the silica or silica-alumina clay.

7. A composition as claimed in any of claims 1 to 6 containing from 10% to 50% by weight of the polar coupling agent based on the weight of the silica or hydrated silica-alumina clay.

8. A composition as claimed in any of claims 1 to 7 wherein the active hydrogen atoms of the polar coupling agent are the hydrogen atoms of water, or of hydroxyl or primary or secondary amine groups.

9. A composition as claimed in claim 8 wherein the polar coupling agent is water, or an organic diol or diamine containing up to 10 carbon atoms.

10. A composition as claimed in any of claims 1 to 9 having a yield point of from 100 to 10,000 dynes per square centimeter.

11. A composition as claimed in any of claims 1 to 9 having a yield point of at least 400 dynes per square centimeter.

12. A composition as claimed in any of claims 1 to 11 having a high shear viscosity of from 1,000 to 100,000 centipoise.

13. A composition as claimed in any of claims 1 to 12 wherein the polymerisable acrylate ester monomer is a polyacrylate ester monomer or a monoacrylate ester monomer in which the alcoholic moiety contains a polar group which is a labile hydrogen atom, a heterocyclic ring or a hydroxy, amino, cyano or halogen polar group.

14. A composition as claimed in any of claims 1 to 13 additionally containing an amine accelerator of free radical polymerisation.

15. A composition as claimed in any of claims 1 to 14, additionally containing an organic sulphimide.

16. An anaerobic composition which is gelled and non-flowable when at rest substantially as hereinbefore described with reference to any of the Examples.

17. A process for the production of an anaerobic composition as claimed in any of claims 1 to 16 which comprises uniformly distributing the silica or hydrated silica-alumina clay and the polar coupling agent therefor in the remaining components of the anaerobic composition and allowing the mixture to stand until it forms a gel-like substance.

18. An article for assembly with a mating second article at least a portion of the

engagement area of the article being coated with a composition as claimed in any of claims 1 to 16.

19. An article as claimed in claim 18 wherein the article is a threaded fastener or a threaded pipe.

ELKINGTON AND FIFE,  
Chartered Patent Agents,  
High Holborn House,  
52/54 High Holborn,  
London WC1V 6SH,  
Agents for the Applicants.

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